

Molecular Characterization of Organic Nitrogen in Aerosols Using High Resolution Mass Spectrometry

J. Smith, A. Laskin, J. Laskin

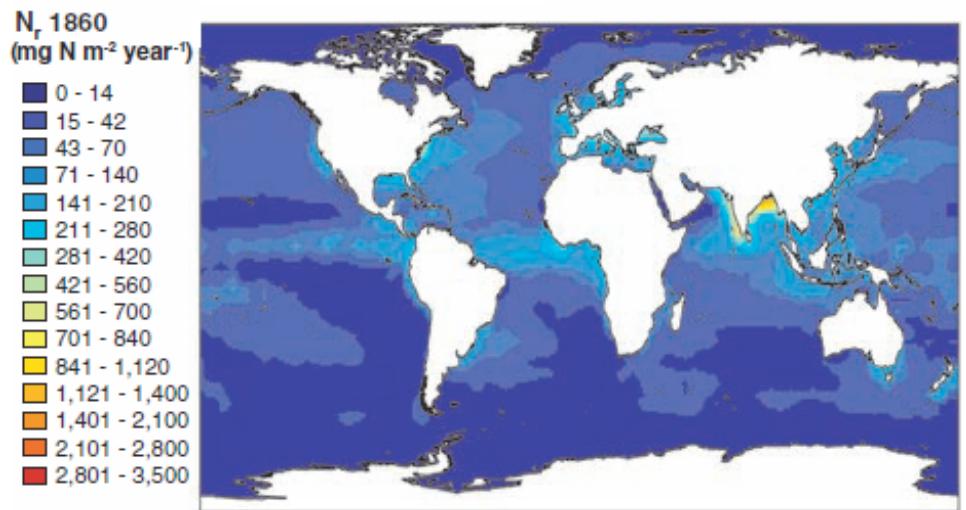
***Environmental Molecular Science Laboratory
Pacific Northwest National Laboratory***



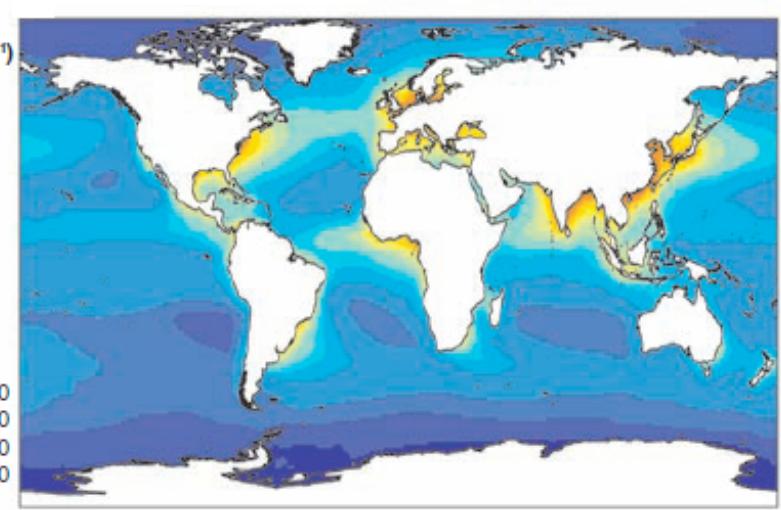
Deposition of Atmospheric Anthropogenic Nitrogen into Oceans

Duce et al, *Science*, 320, 893-897 (2008)

Year 1860



Year 2000



- ❖ 10-100 fold increase over last century
- ❖ Estimated 30% of Organic Nitrogen (ON)

ON in Biomass Burning Aerosol



Ponderosa Pine Needles
and Sticks

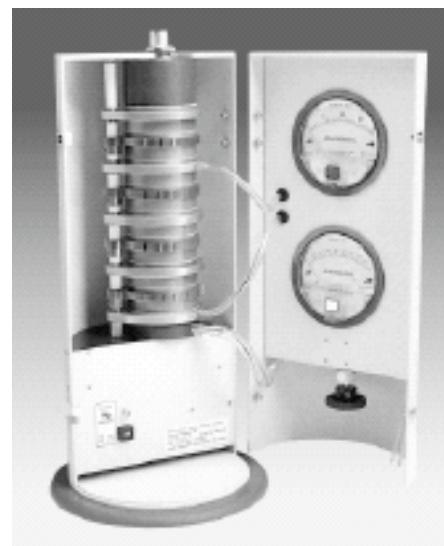


Southern Pine Needles

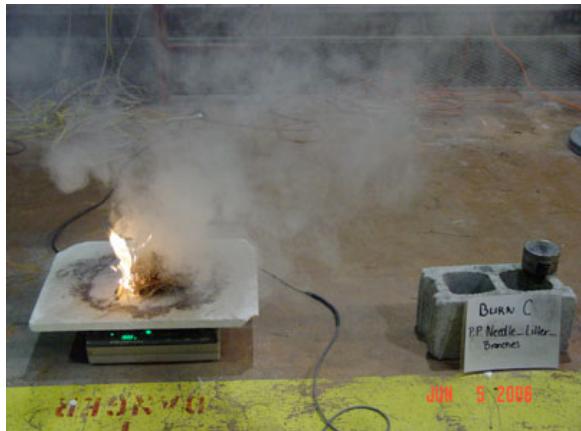


Southern California ceanothus

Collection



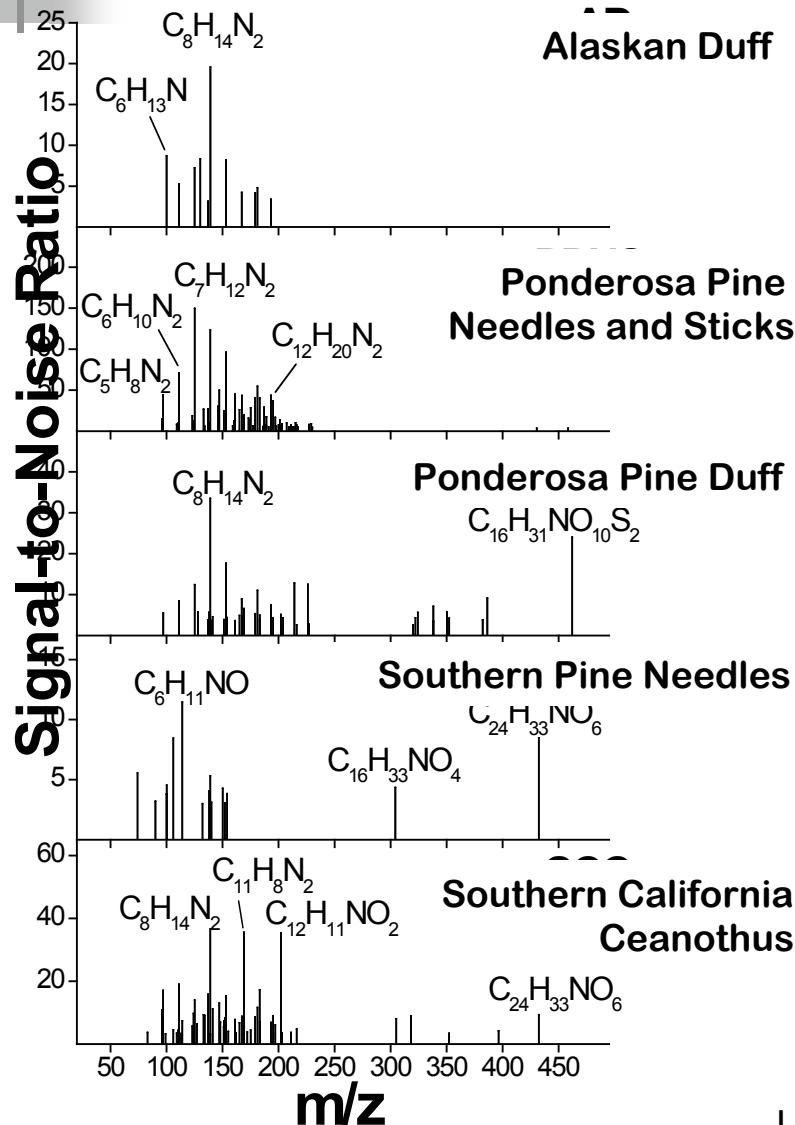
Burn



Extraction & Analysis



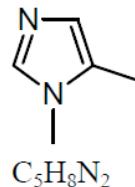
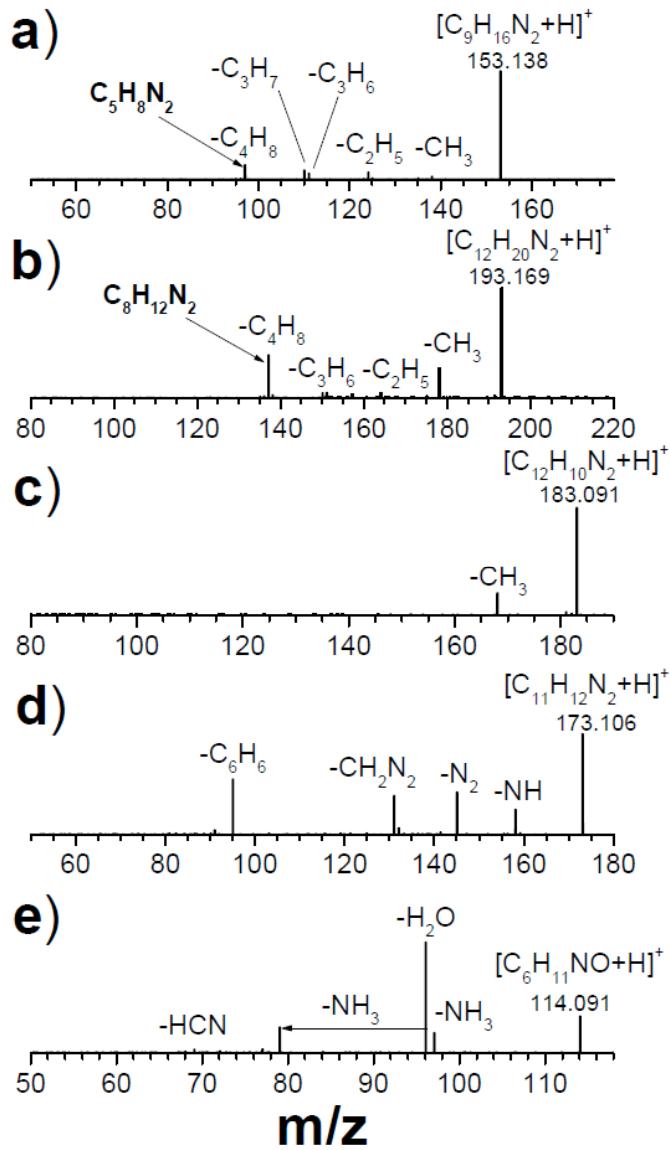
ON in Biomass Burning Aerosol



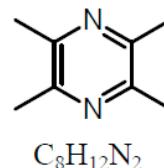
- ❖ ON account for 10-20% of all assigned peaks in ESI-MS spectra
- ❖ Significant variation between samples
- ❖ Dominant compounds with two nitrogen atoms
- ❖ High Double Bond Equivalent (DBE) values of 3-9

A. Laskin, J. Smith, J. Laskin *EST*, 2009, in press
J. Smith, A. Laskin, J. Laskin *Anal. Chem.*, 2009, 81 (4),
1512-1521

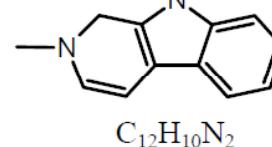
MS/MS Identification of Alkaloids



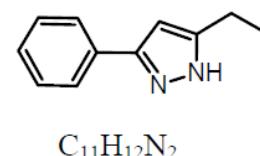
dimethylimidazole



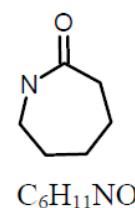
tetramethylpyrazine



β -carboline



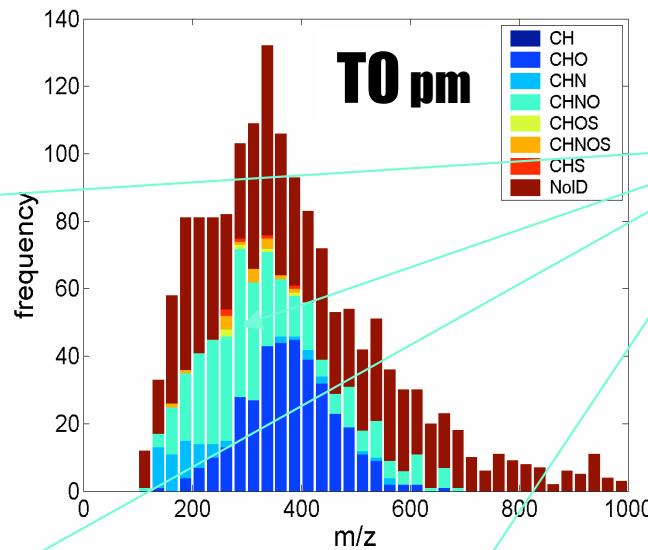
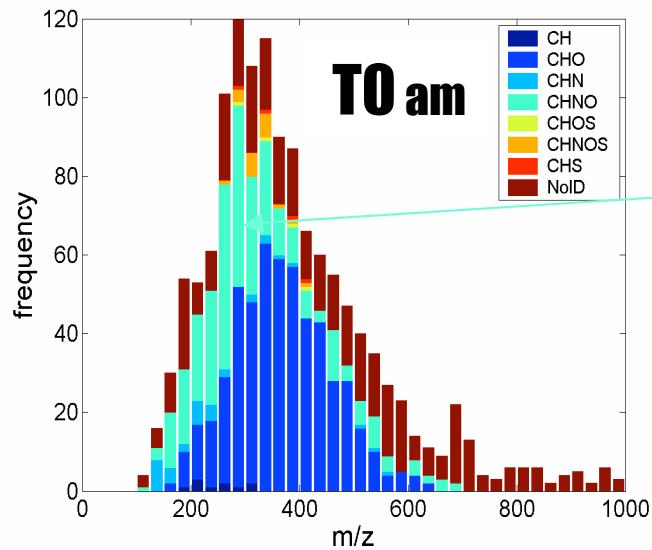
substituted phenylpyrazole



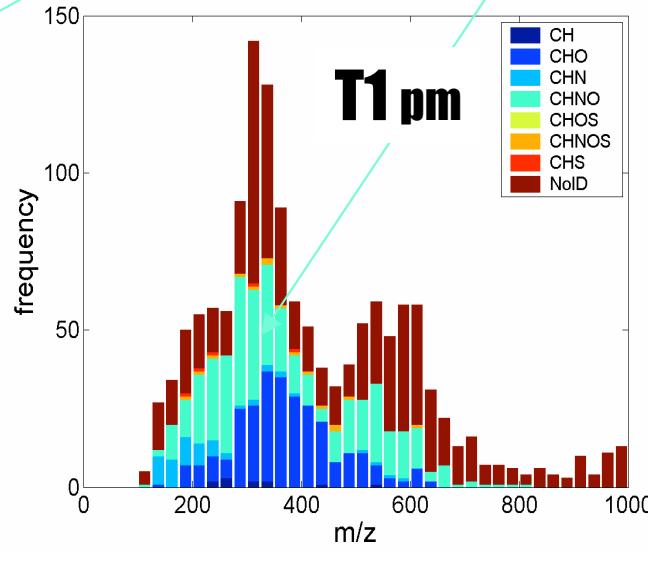
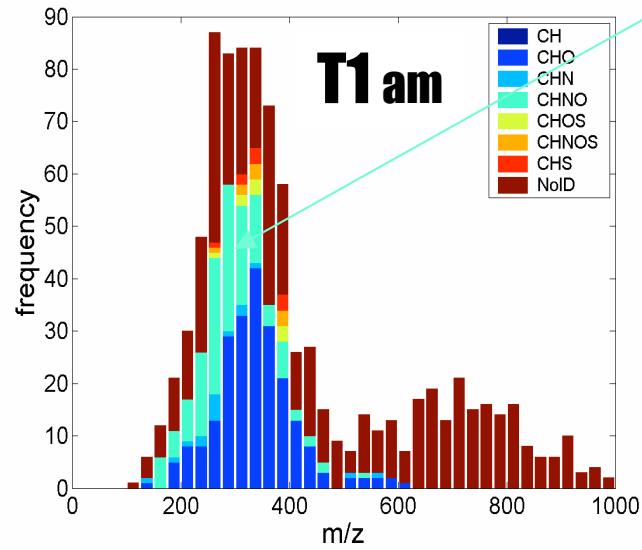
ε -caprolactam

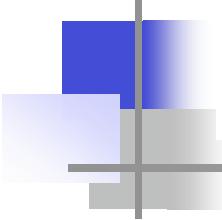
Organic Nitrogen in MILAGRO samples

R. Moffet, M. Gilles (*LBNL*); N. Marley, J. Gaffney (*UALR*);
A. Laskin, J. Laskin (*PNNL*)



CHNO
20-30%
of detected
peaks





SUMMARY

- ❖ High Res. ESI/MS spectra provide distinct, sample specific, characteristic peaks of ON compounds.
- ❖ N-heterocyclic compounds (Alkaloids) comprise a substantial fraction of ON in biomass burning aerosol.
- ❖ Alkaloids may play a significant role in dry and wet deposition of fixed nitrogen.
- ❖ Unrecognized source of basicity in aerosols.

ONGOING WORK

- ❖ Molecular characterization of ON in MILAGRO samples
- ❖ Quantitative analysis of ON and other compounds in PILS collected samples
- ❖ Development of data analysis and informatics tools for digesting HR-MS data